Supporting Information

Efficient Heterogeneous Catalysis by Pendant Metalloporphyrin-functionalized Polythiophenes for Electrochemical Carbon Dioxide Reduction

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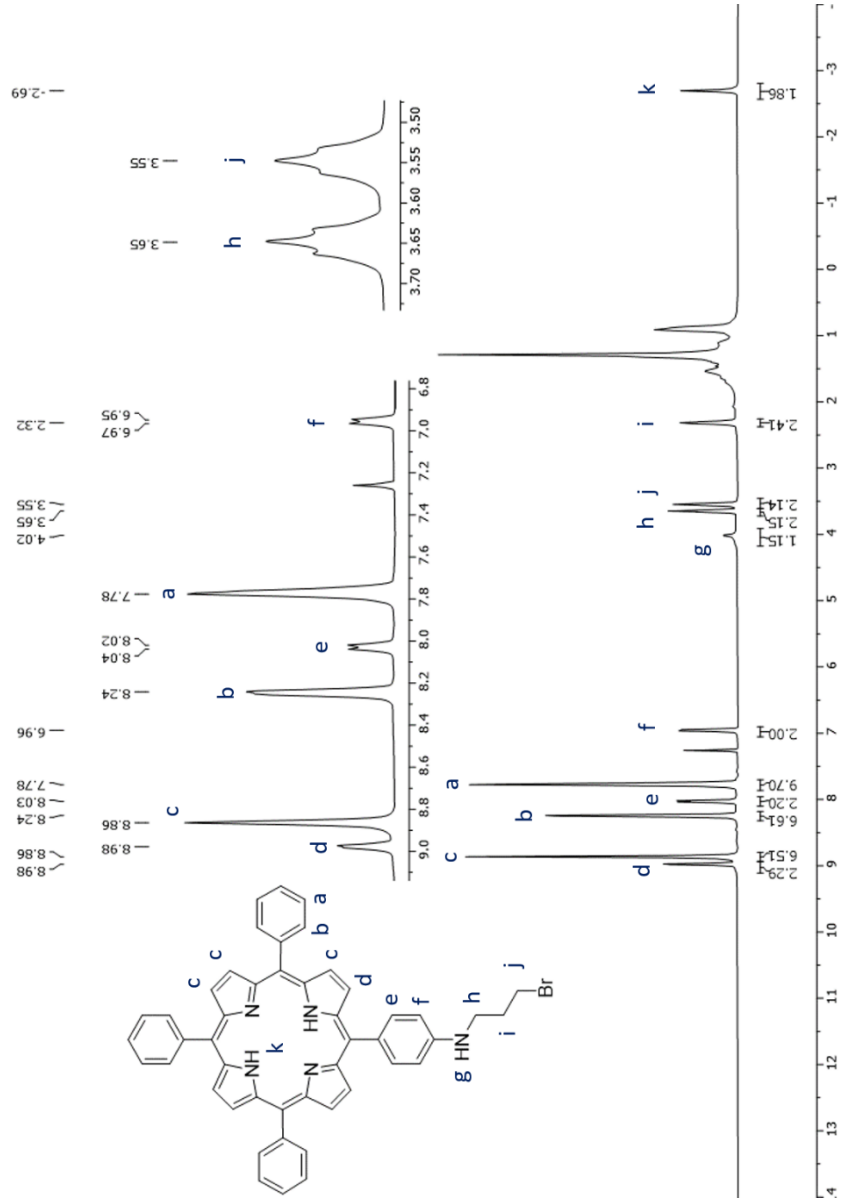


Figure S1 ^{1}H-NMR spectrum of compound **3** in $CDCl_3$.

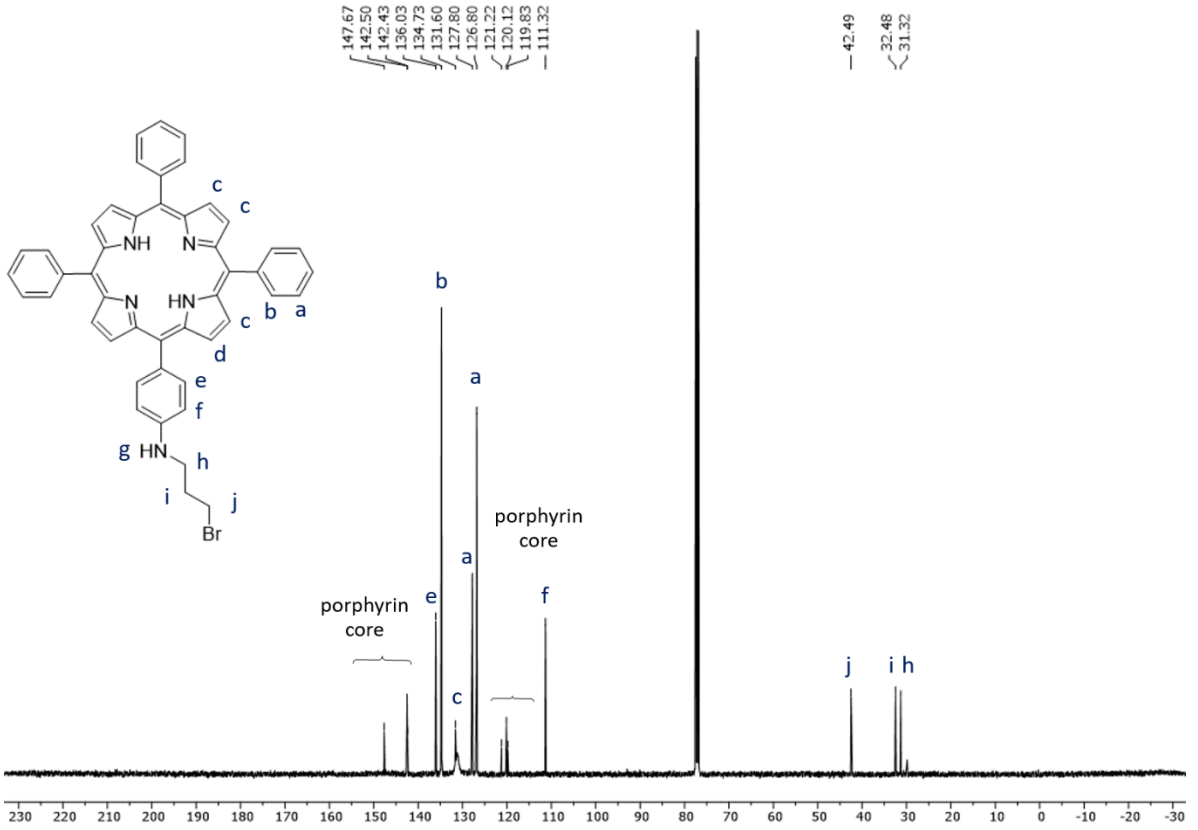


Figure S2 ^{13}C-NMR spectrum of compound **3** in $CDCl_3$.

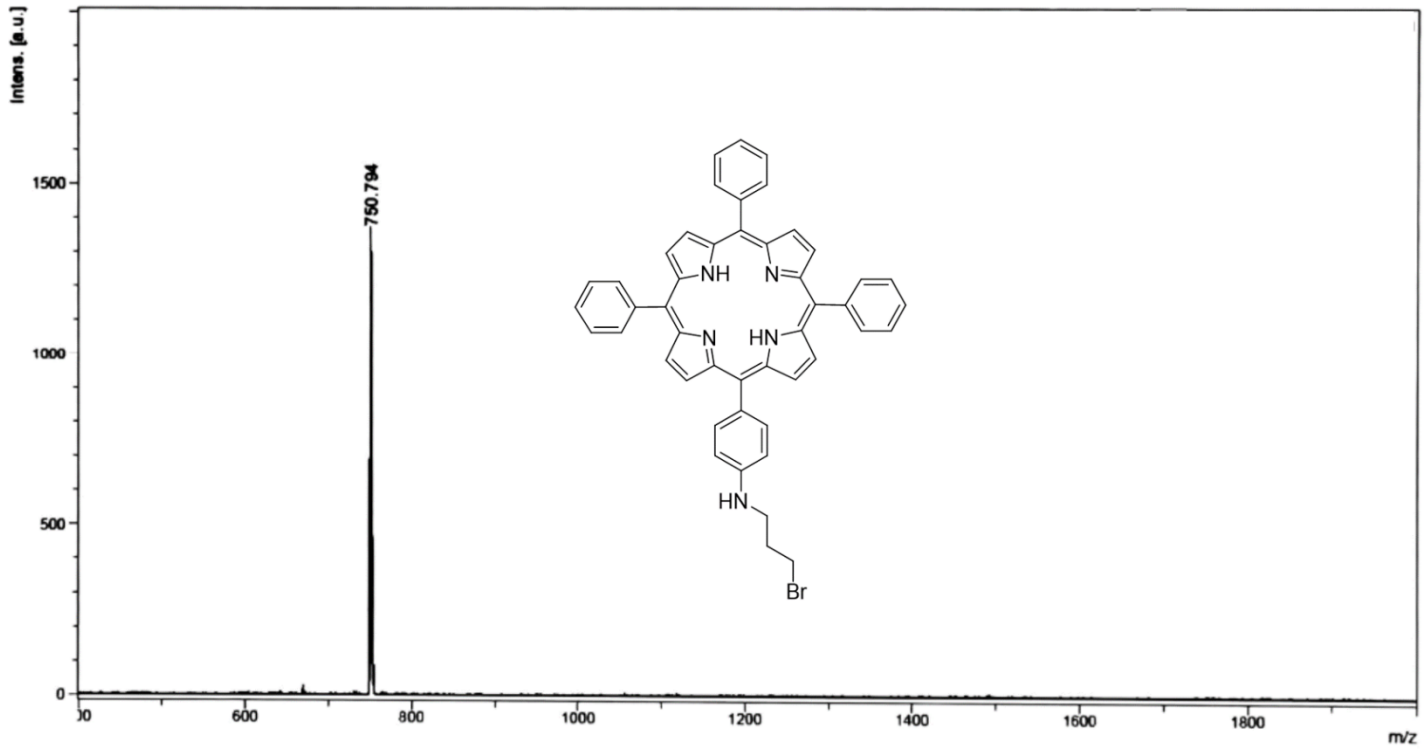


Figure S3 MALDI-TOF mass spectrum of compound **3**.

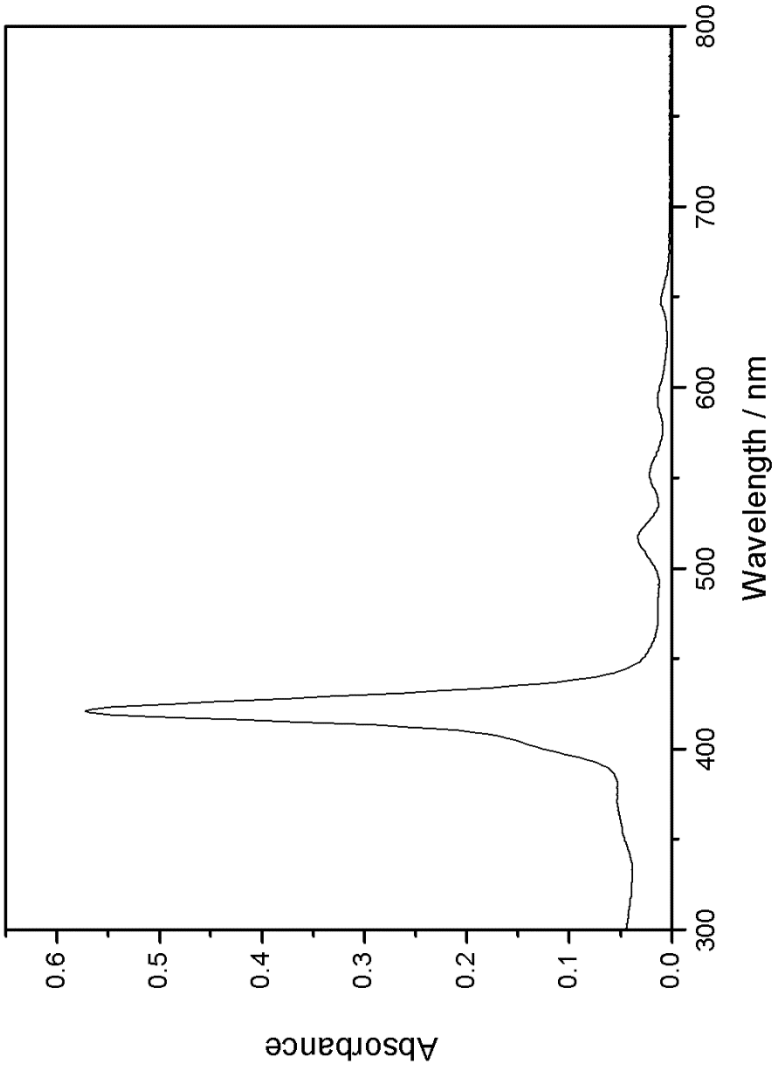


Figure S4 Absorption spectrum of compound **3** in toluene.

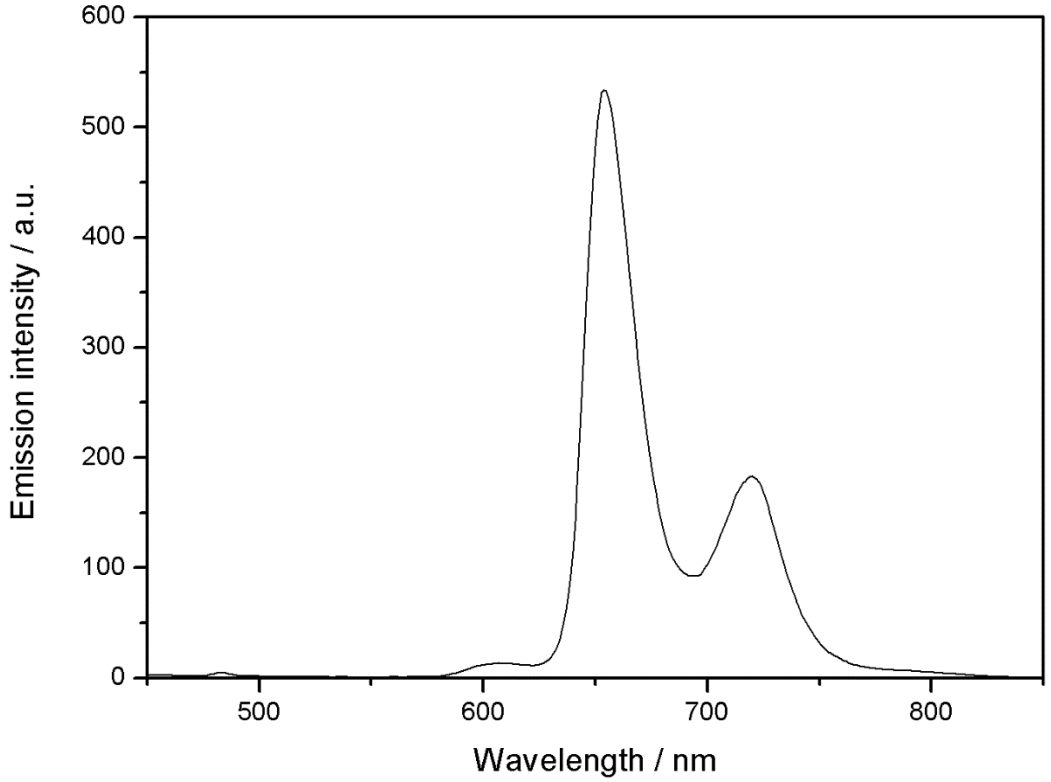


Figure S5 Emission spectrum of compound **3** in toluene (λ_{ex} = 421 nm).

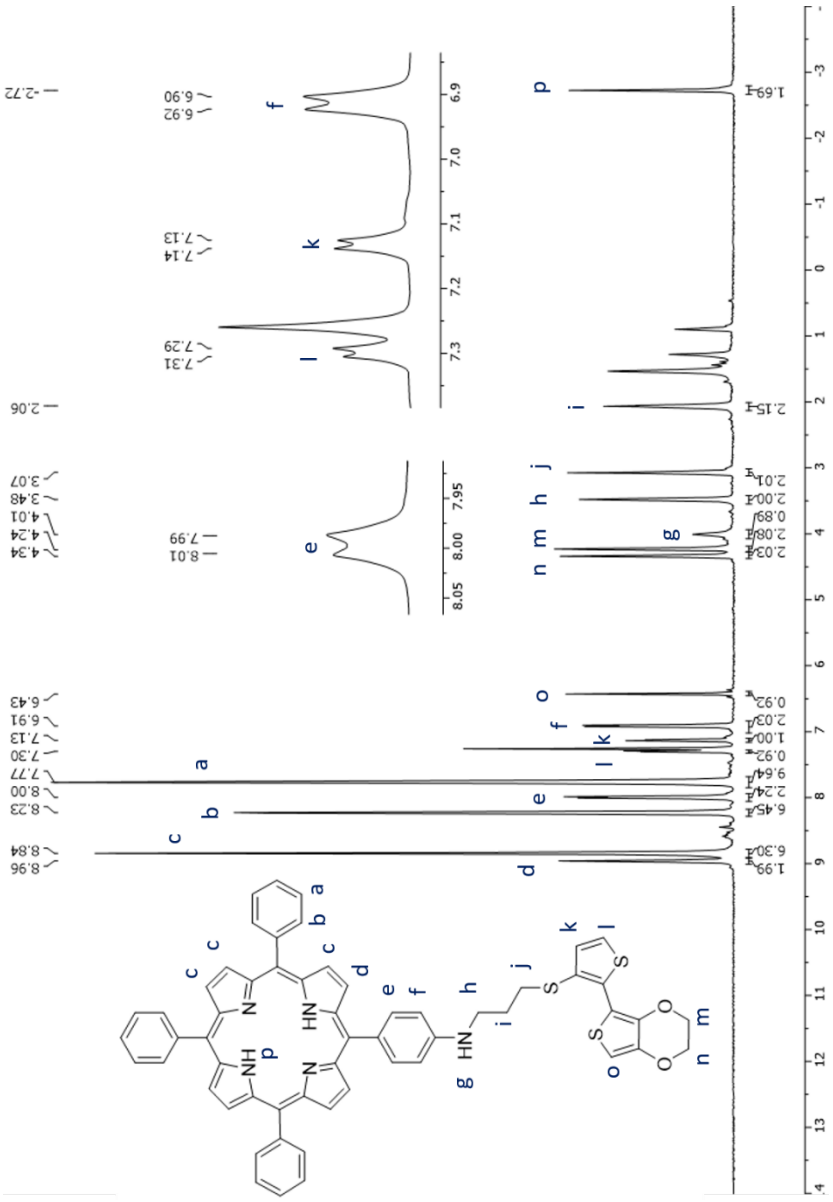


Figure S6 ^{1}H-NMR spectrum of compound **1** in $CDCl_3$.

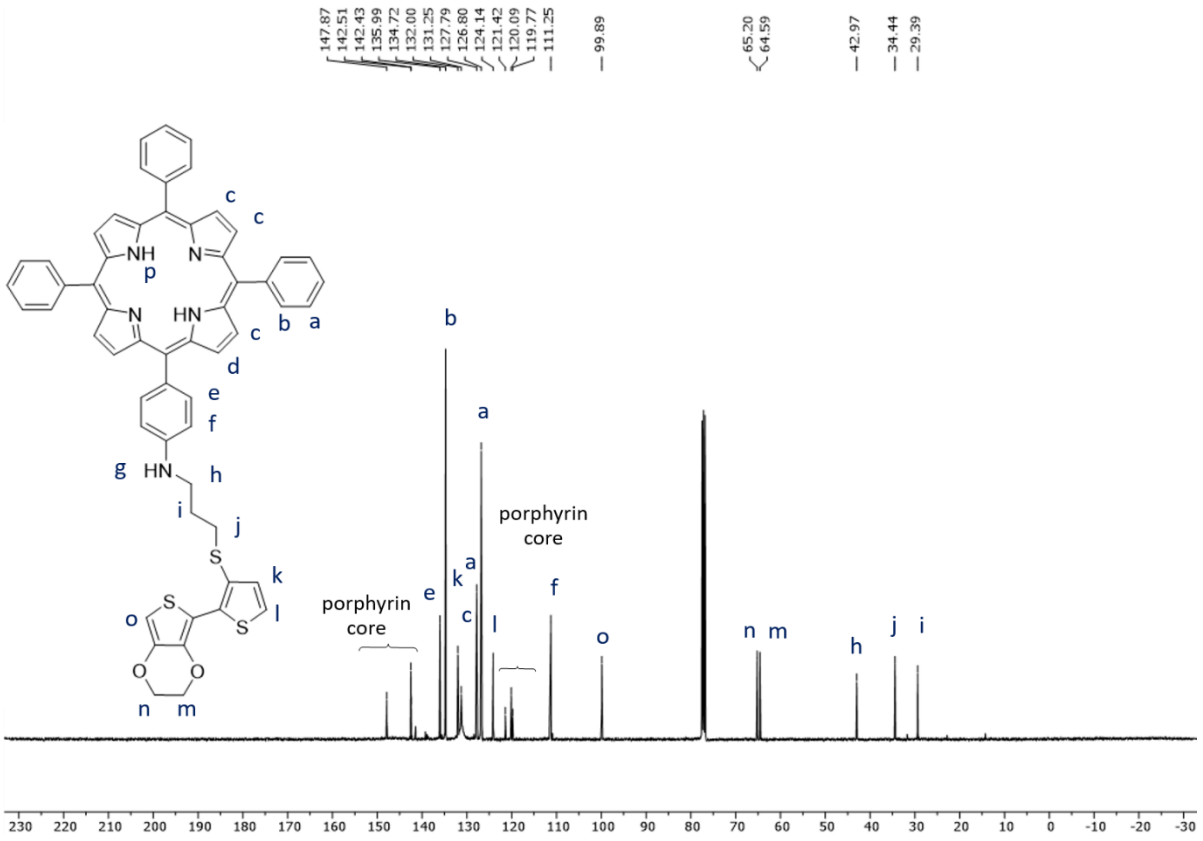
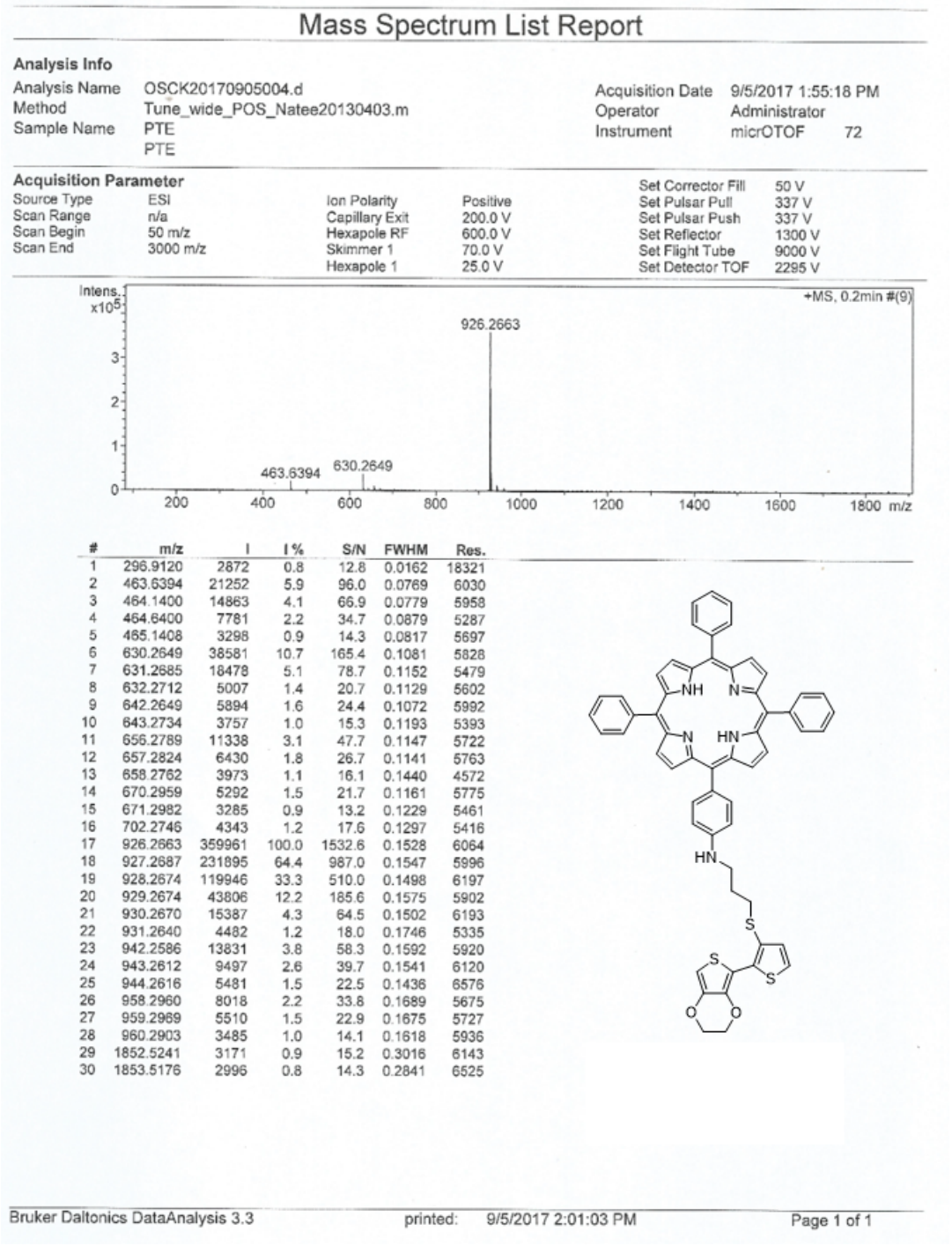


Figure S7 ^{13}C-NMR spectrum of compound **1** in $CDCl_3$.



Mass Spectrum List Report

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Method	Tune_wide_POS_Natee20130403.m	Operator	Administrator
Sample Name	PTE	Instrument	micrOTOF 72
	PTE		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	200.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	600.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	70.0 V	Set Reflector	1300 V
		Hexapole 1	25.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V

#	m/z	I	I %	S/N	FWHM	Res.
1	296.9120	2872	0.8	12.8	0.0162	18321
2	463.6394	21252	5.9	96.0	0.0769	6030
3	464.1400	14863	4.1	66.9	0.0779	5958
4	464.6400	7781	2.2	34.7	0.0879	5287
5	465.1408	3298	0.9	14.3	0.0817	5697
6	630.2649	38581	10.7	165.4	0.1081	5828
7	631.2685	18478	5.1	78.7	0.1152	5479
8	632.2712	5007	1.4	20.7	0.1129	5602
9	642.2649	5894	1.6	24.4	0.1072	5992
10	643.2734	3757	1.0	15.3	0.1193	5393
11	656.2789	11338	3.1	47.7	0.1147	5722
12	657.2824	6430	1.8	26.7	0.1141	5763
13	658.2762	3973	1.1	16.1	0.1440	4572
14	670.2959	5292	1.5	21.7	0.1161	5775
15	671.2982	3285	0.9	13.2	0.1229	5461
16	702.2746	4343	1.2	17.6	0.1297	5416
17	926.2663	359961	100.0	1532.6	0.1528	6064
18	927.2687	231895	64.4	987.0	0.1547	5996
19	928.2674	119946	33.3	510.0	0.1498	6197
20	929.2674	43806	12.2	185.6	0.1575	5902
21	930.2670	15387	4.3	64.5	0.1502	6193
22	931.2640	4482	1.2	18.0	0.1746	5335
23	942.2586	13831	3.8	58.3	0.1592	5920
24	943.2612	9497	2.6	39.7	0.1541	6120
25	944.2616	5481	1.5	22.5	0.1436	6576
26	958.2960	8018	2.2	33.8	0.1689	5675
27	959.2969	5510	1.5	22.9	0.1675	5727
28	960.2903	3485	1.0	14.1	0.1618	5936
29	1852.5241	3171	0.9	15.2	0.3016	6143
30	1853.5176	2996	0.8	14.3	0.2841	6525

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Figure S8 HR-ESI mass spectrum of compound **1**.

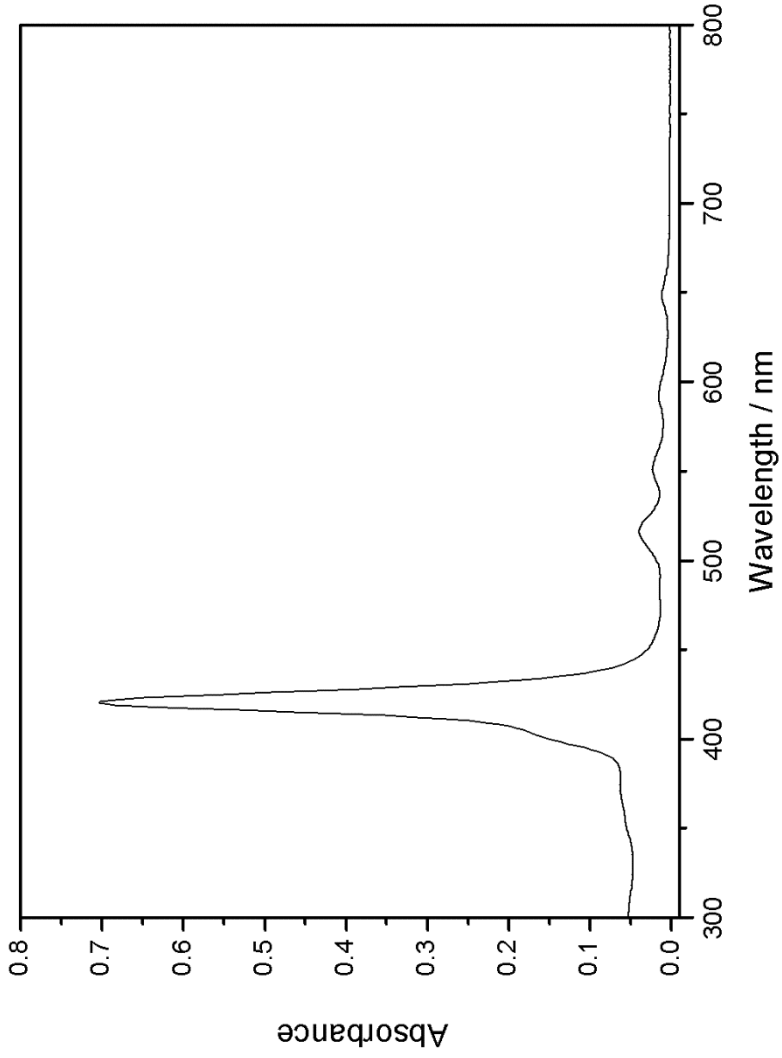

Figure S9 Absorption spectrum of compound **1** in toluene.

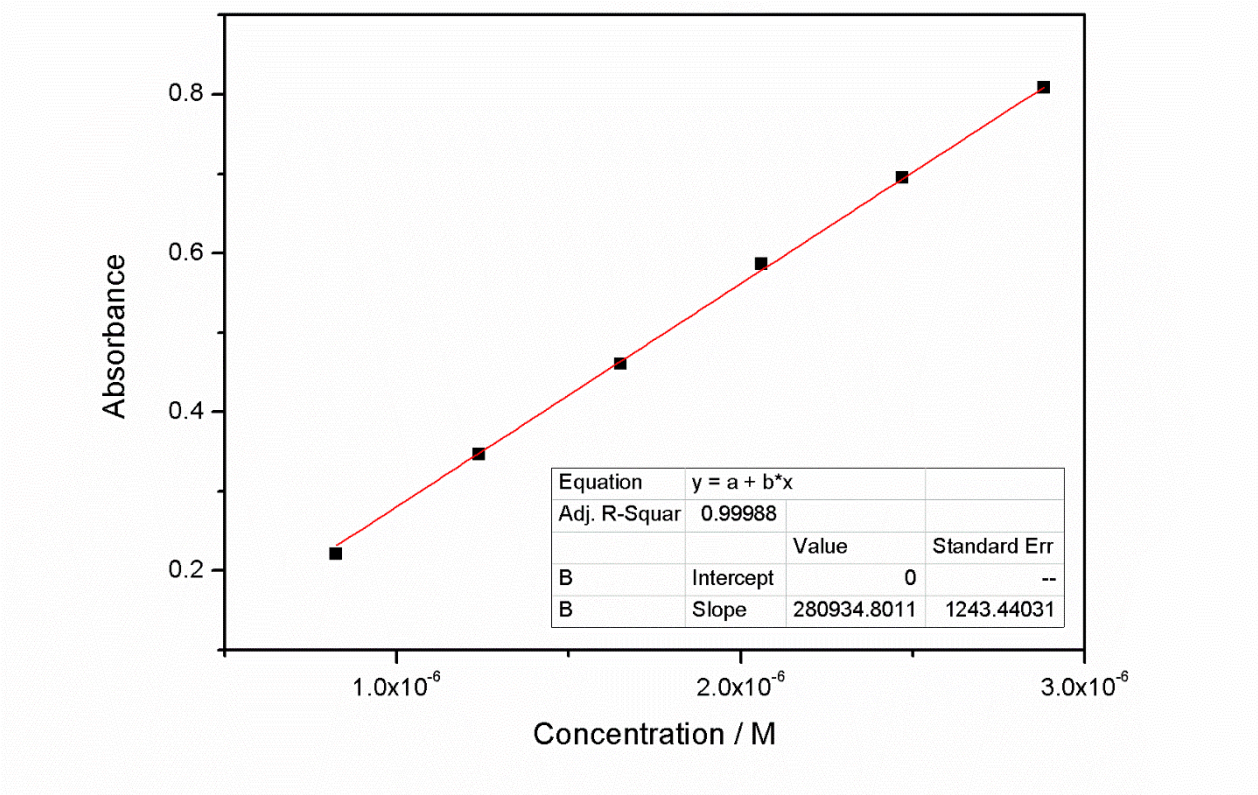

Figure S10 Calibration curve of **1** in toluene (λ_{max} = 422 nm).

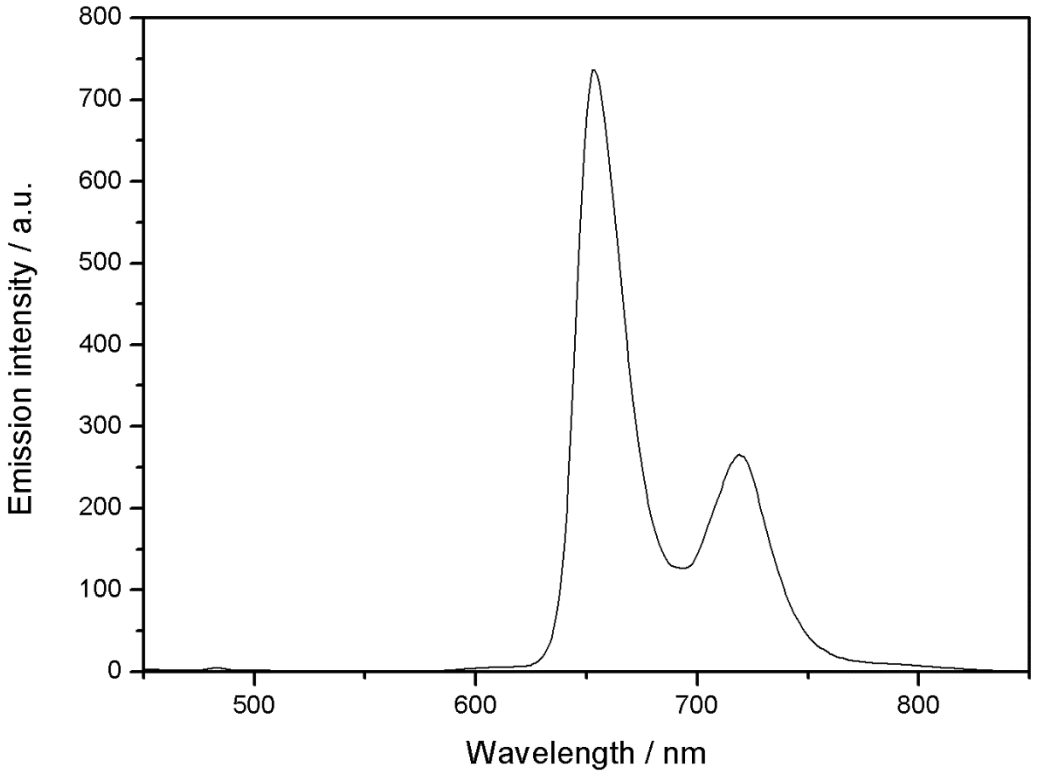

Figure S11 Emission spectrum of compound **1** in toluene (λ_{ex} = 422 nm).

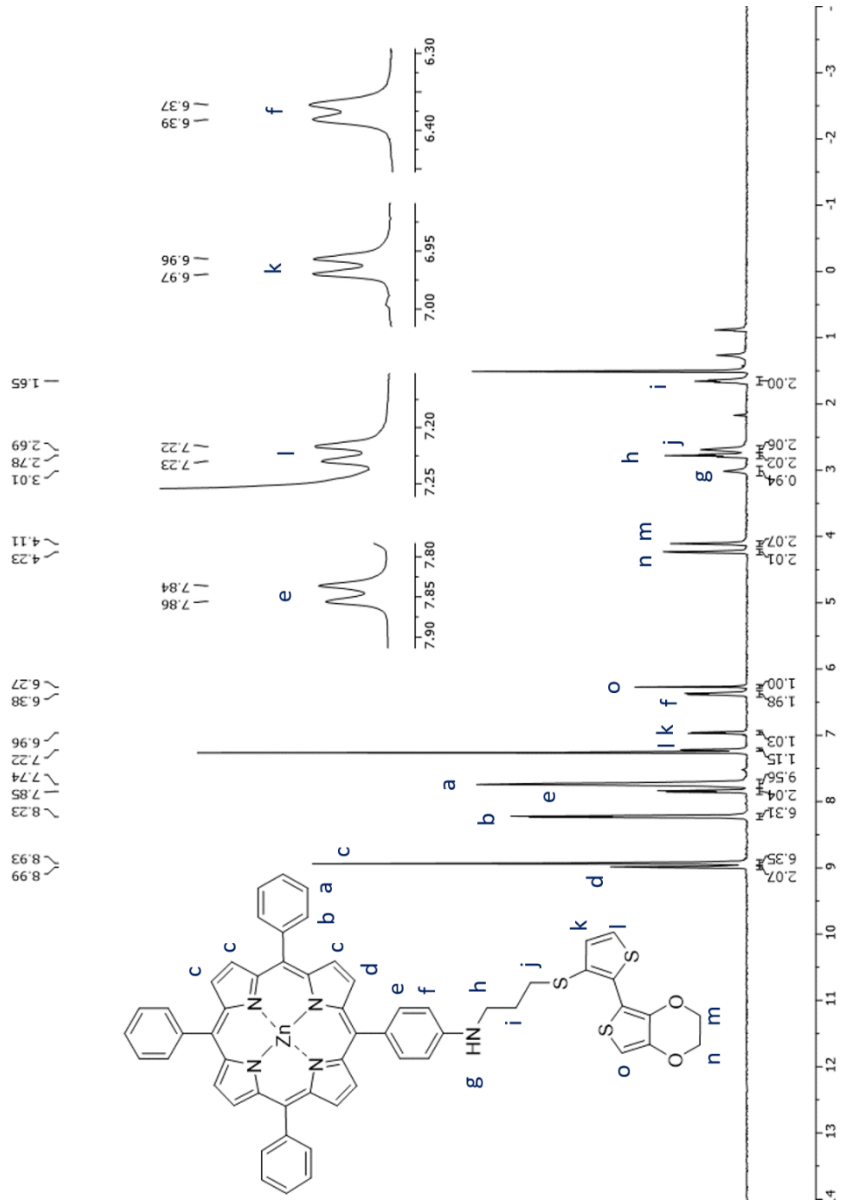

Figure S12 ^{1}H-NMR spectrum of compound **Zn-1** in $CDCl_3$.

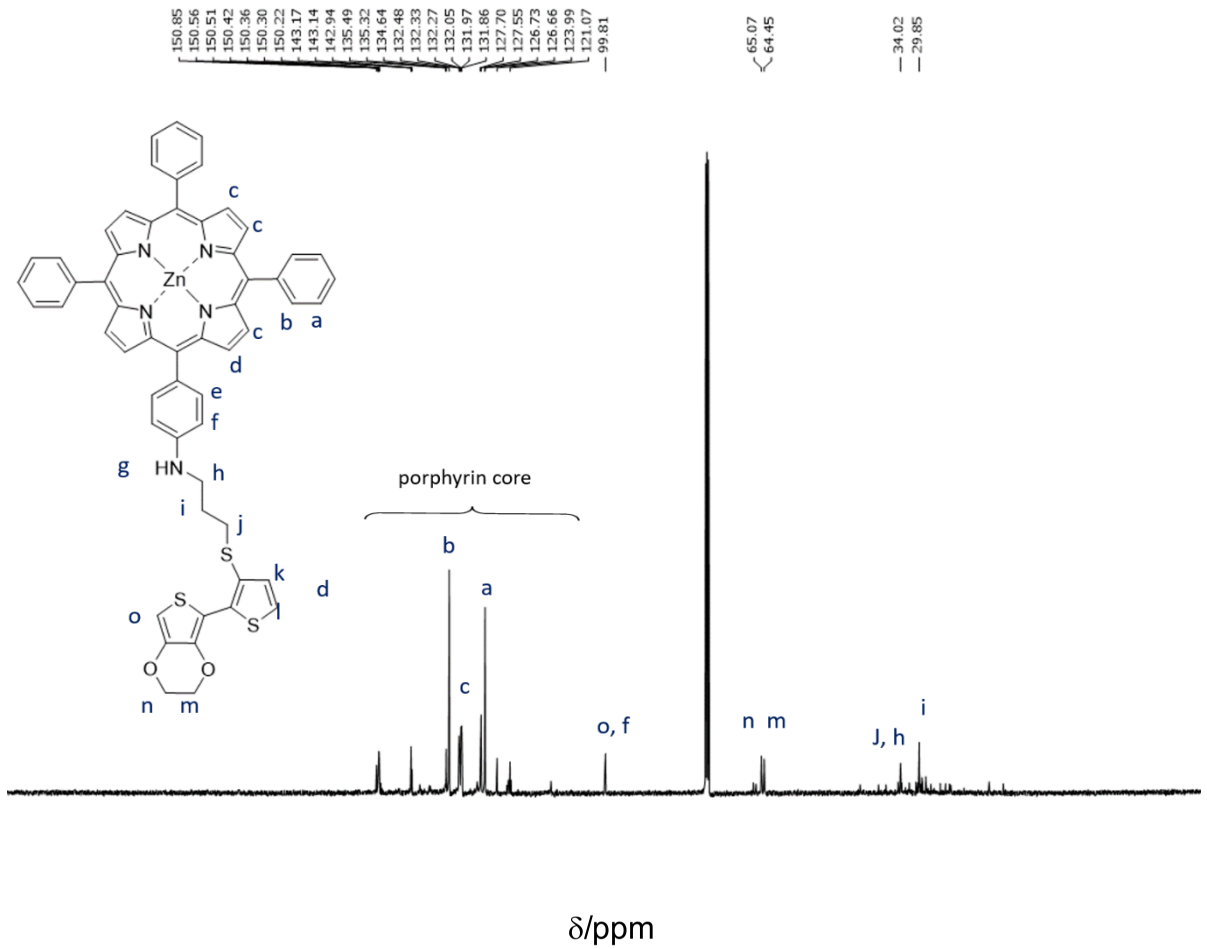

Figure S13 ^{13}C-NMR spectrum of compound **Zn-1** in $CDCl_3$.

Mass Spectrum List Report

Analysis Info

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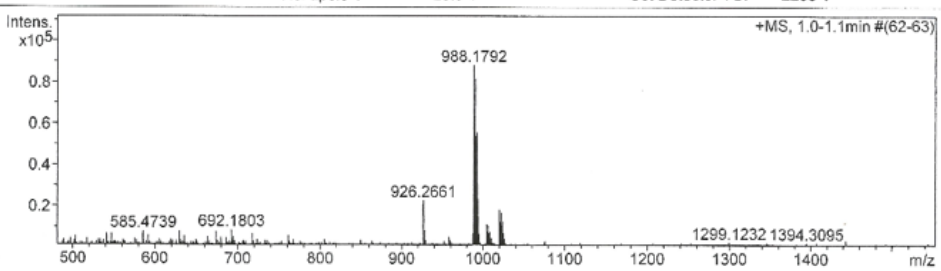
Method	Tune_wide_POS_Natee20130403.m	Operator	Administrator
Sample Name	Zn-PTE Zn-PTE	Instrument	micrOTOF 72

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	200.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	600.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	70.0 V	Set Reflector	1300 V
		Hexapole 1	25.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	FWHM	Res.
1	413.2669	11769	13.3	28.5	0.0753	5491
2	449.3601	21430	24.3	50.3	0.0838	5360
3	450.3620	6905	7.8	15.6	0.0754	5974
4	547.3768	6727	7.6	13.7	0.0913	5998
5	585.4739	7867	8.9	16.2	0.1124	5211
6	629.4967	7738	8.8	15.9	0.1231	5113
7	673.5221	7727	8.8	16.0	0.1154	5838
8	692.1803	8495	9.6	17.7	0.0921	7514
9	717.5540	6745	7.6	13.9	0.1275	5629
10	926.2661	22940	26.0	50.9	0.1610	5753
11	927.2655	15585	17.7	34.2	0.1602	5789
12	928.2684	8314	9.4	17.6	0.1580	5874
13	988.1792	88265	100.0	210.6	0.1728	5719
14	989.1816	63771	72.2	152.0	0.1700	5819
15	990.1780	81816	92.7	195.5	0.1678	5900
16	991.1799	54223	61.4	129.3	0.1685	5882
17	992.1772	55711	63.1	133.0	0.1760	5637
18	993.1783	31139	35.3	73.9	0.1785	5565
19	994.1775	14981	17.0	34.9	0.1777	5595
20	1004.1756	11268	12.8	26.2	0.1764	5692
21	1005.1810	7947	9.0	18.1	0.1703	5901
22	1006.1732	10766	12.2	25.1	0.1701	5916
23	1007.1730	6766	7.7	15.3	0.1792	5622
24	1008.1729	7638	8.7	17.4	0.1921	5249
25	1020.1694	18264	20.7	44.0	0.1743	5853
26	1021.1760	12469	14.1	29.7	0.1737	5879
27	1022.1693	17000	19.3	41.0	0.1758	5816
28	1023.1701	10727	12.2	25.4	0.1896	5396
29	1024.1672	12751	14.4	30.5	0.1754	5838
30	1025.1679	6887	7.8	15.9	0.1797	5705

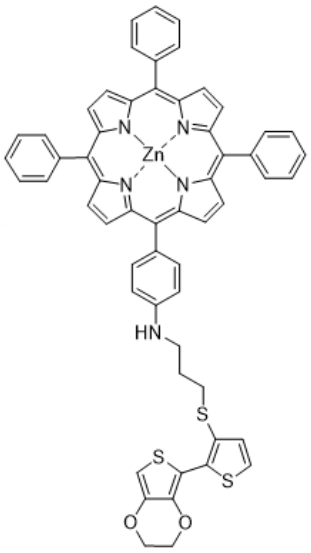


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Figure S14 HR-ESI mass spectrum of compound **Zn-1**.

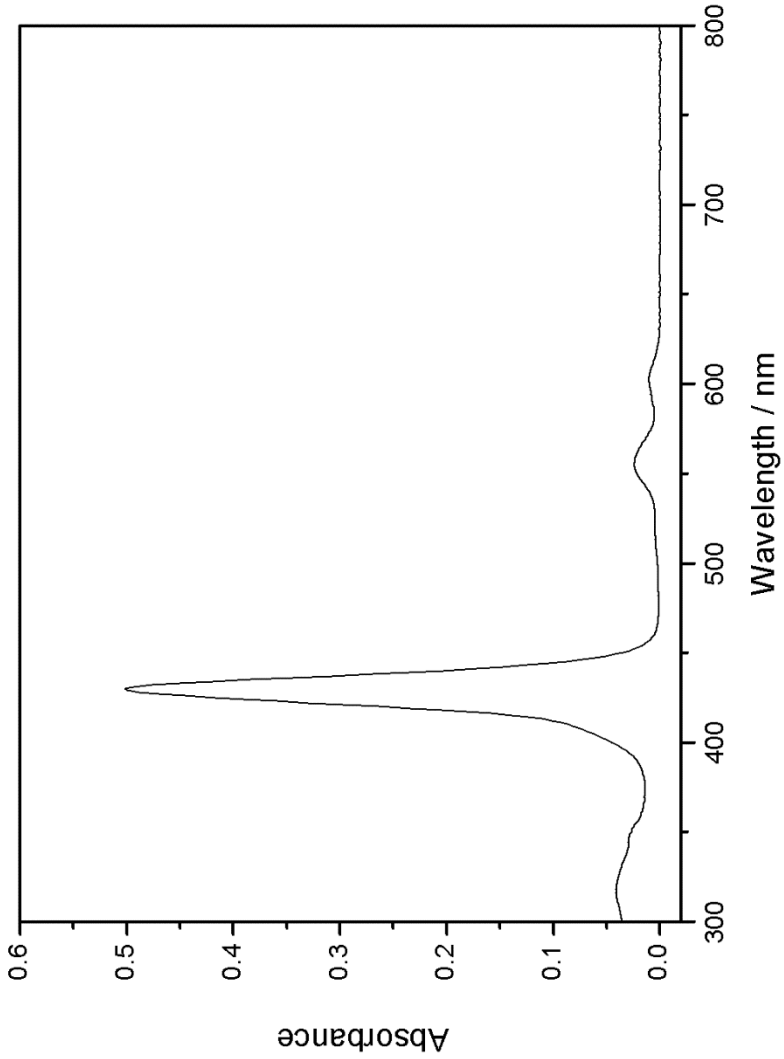

Figure S15 Absorption spectrum of compound **Zn-1** in toluene.

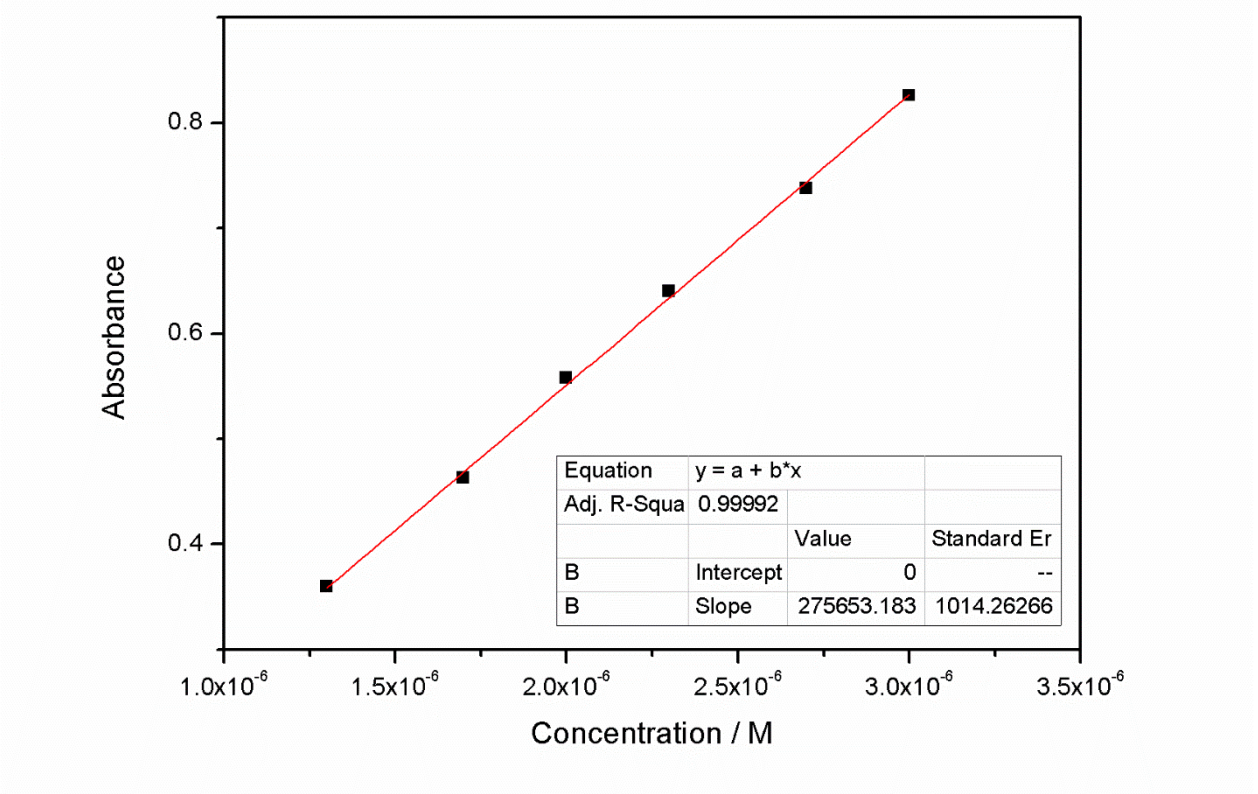

Figure S16 Calibration curve of **Zn-1** in toluene (λ_{max} = 429 nm).

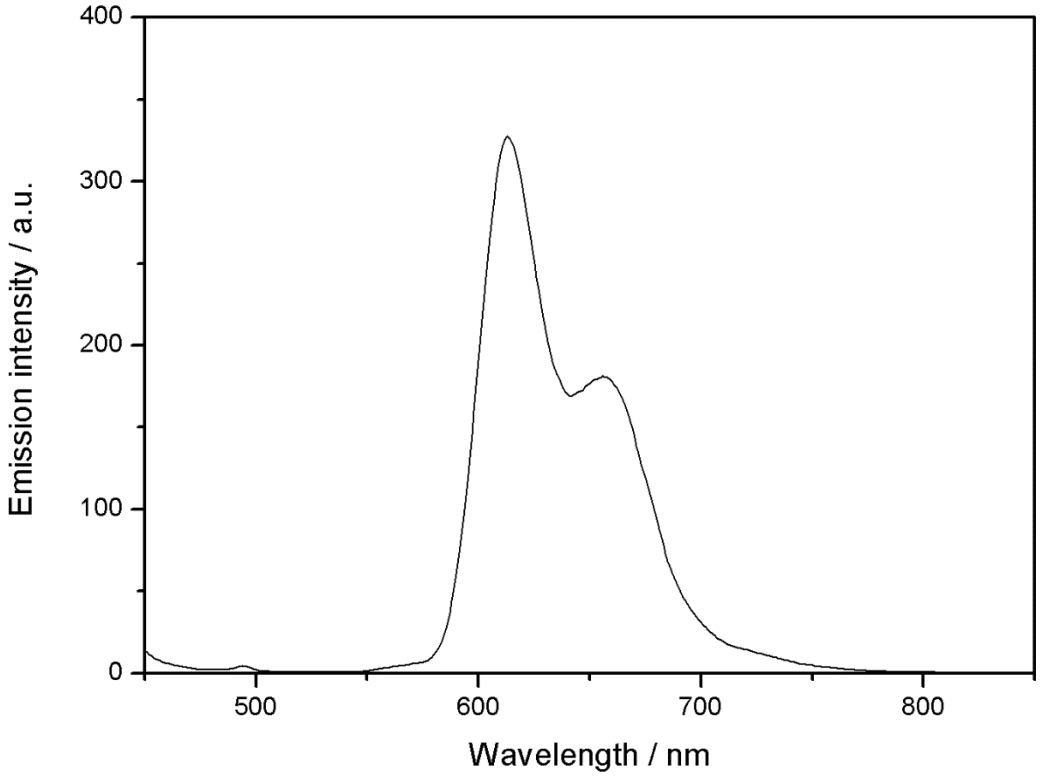

Figure S17 Emission spectrum of compound **Zn-1** in toluene (λ_{ex} = 430 nm).

Mass Spectrum List Report

Analysis Info

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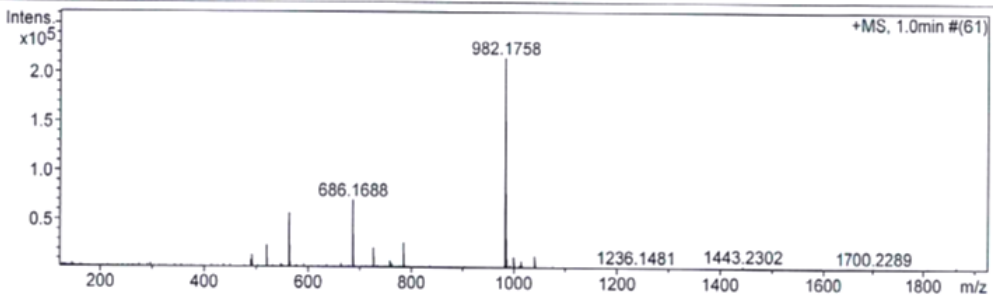
Method	Tune_wide_POS_Natee20130403.m	Operator	Administrator
Sample Name	CoPTE	Instrument	micrOTOF 72
	CoPTE		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	200.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	600.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	70.0 V	Set Reflector	1300 V
		Hexapole 1	25.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	FWHM	Res.
1	489.1700	9485	4.4	20.2	0.1047	4674
2	491.5948	14385	6.7	31.2	0.0938	5242
3	492.0976	10258	4.8	21.9	0.1129	4358
4	520.2106	24208	11.2	52.3	0.1134	4589
5	521.2136	10615	4.9	22.2	0.1164	4478
6	563.2511	56666	26.3	122.7	0.1237	4555
7	564.2519	24066	11.2	51.2	0.1152	4900
8	565.2597	6740	3.1	13.3	0.1404	4025
9	663.4547	5672	2.6	10.5	0.1718	3862
10	686.1688	70332	32.7	151.2	0.1406	4881
11	687.1710	35465	16.5	75.3	0.1395	4927
12	688.1699	9273	4.3	18.3	0.1415	4863
13	726.2017	21720	10.1	45.3	0.1423	5104
14	727.2016	12894	6.0	26.1	0.1414	5143
15	758.2081	8825	4.1	17.4	0.1555	4877
16	759.2033	7172	3.3	13.8	0.1629	4661
17	784.2102	27355	12.7	58.7	0.1528	5133
18	785.2115	16031	7.4	33.6	0.1516	5180
19	982.1758	215290	100.0	525.4	0.1920	5116
20	983.1775	151832	70.5	370.3	0.1904	5164
21	984.1755	78033	36.2	189.7	0.1985	4959
22	985.1763	31717	14.7	76.2	0.2021	4874
23	986.1733	11139	5.2	25.8	0.1857	5310
24	999.1735	13152	6.1	31.0	0.1972	5068
25	1000.1797	9084	4.2	21.0	0.1956	5114
26	1014.1702	8947	4.2	20.9	0.1892	5360
27	1015.1706	5688	2.6	12.7	0.1902	5336
28	1040.1811	13922	6.5	34.0	0.2074	5016
29	1041.1856	10243	4.8	24.6	0.1961	5310
30	1042.1838	6633	3.1	15.5	0.1781	5852

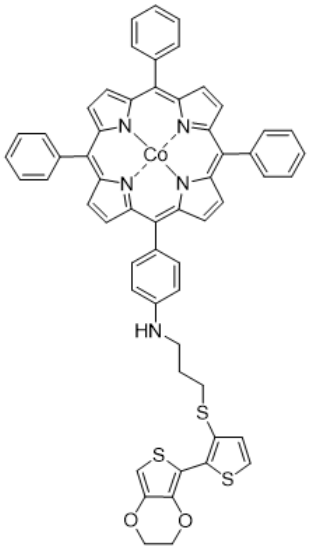


Figure S18 HR-ESI mass spectrum of compound **Co-1**.

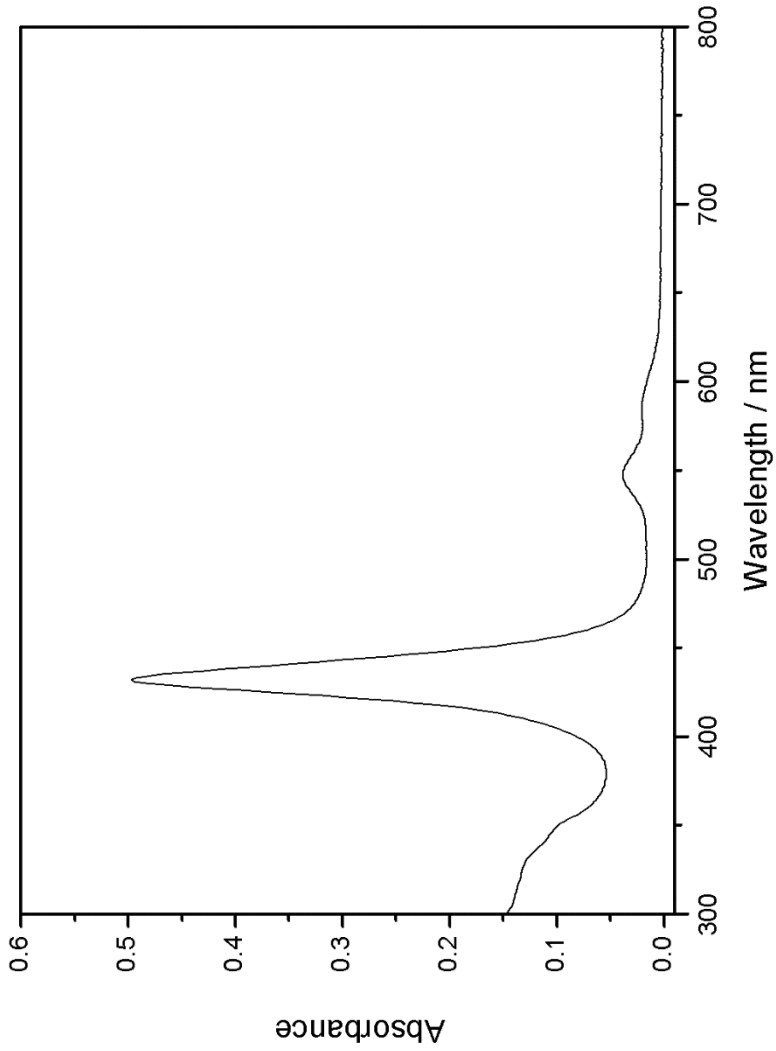


Figure S19 Absorption spectrum of compound **Co-1** in toluene.

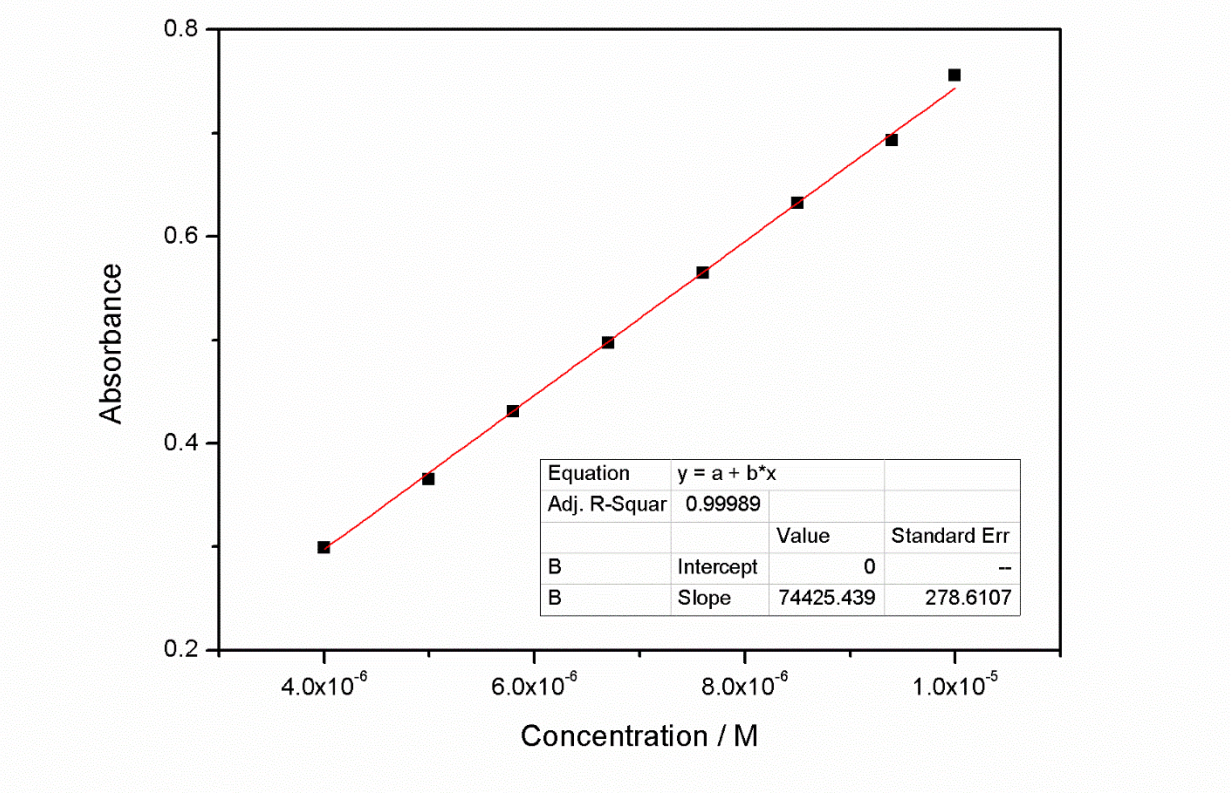


Figure S20 Calibration curve of **Co-1** in toluene (λ_{max} = 432 nm).

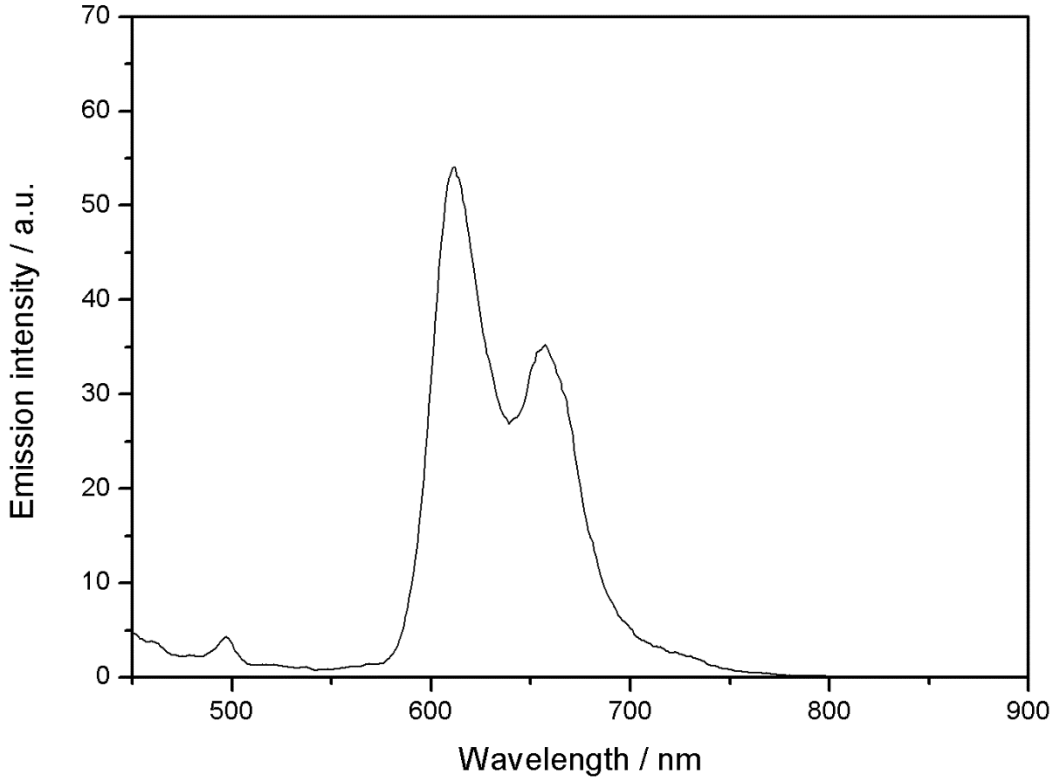


Figure S21 Emission spectrum of compound **Co-1** in toluene (λ_{ex} = 432 nm).

Table S1 TON, TOF and %FE for CO formation during a 6-h CPE experiment of ECR of CO_2 under catalysis of **poly(Co-1)**/carbon paper

Time (h)	**TON** ($\times 10^3$)	**TOF / s^{-1}**	**%FE**
0.5	1.4	0.8	35.8
1.0	1.2	0.7	36.9
1.5	1.2	0.7	36.9
2.0	1.2	0.6	35.2
2.5	1.1	0.6	35.4
3.0	1.1	0.6	35.5
3.5	1.1	0.6	35.7
4.0	1.0	0.6	35.5
4.5	1.1	0.6	36.1
5.0	1.1	0.6	35.3
5.5	1.1	0.7	35.2
6.0	1.2	0.6	36.0
Average	$1.4\times10^{4\,a}$	0.6	35.8

[a] A sum value

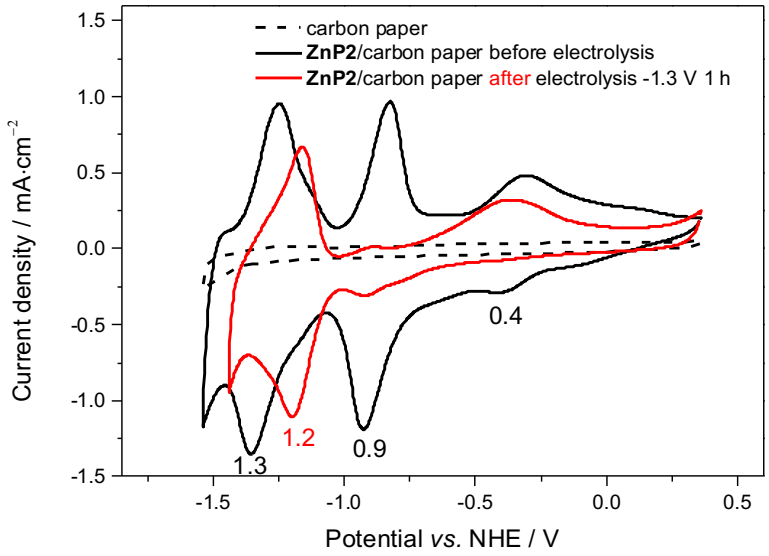


Figure S22 Cyclic voltammograms of the pre- and post-electrolysis **poly(Zn-1)**/carbon paper samples

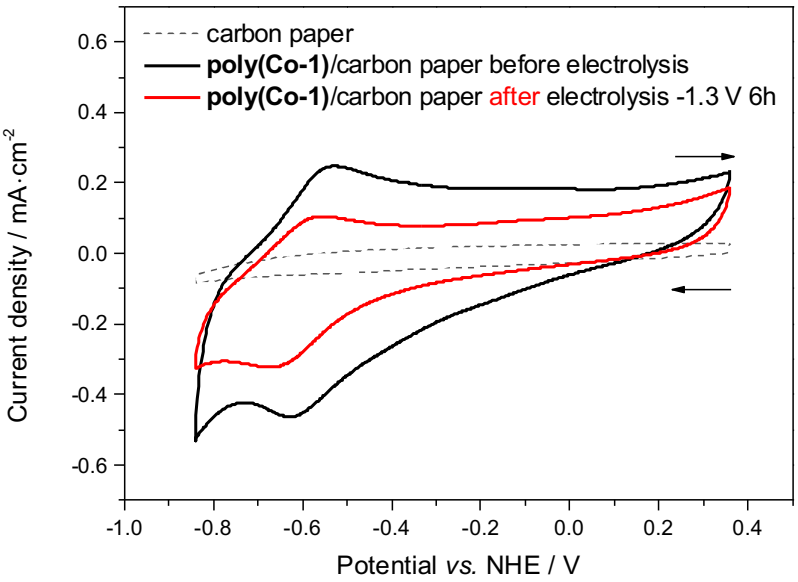


Figure S23 Cyclic voltammograms of the pre- and post-electrolysis **poly(Co-1)**/carbon paper samples